

Form of uncompensated heat giving rise to a Pfaffian differential form in thermodynamic space

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A form of uncompensated heat is presented which gives rise to a Pfaffian differential form for a non-equilibrium extension of equilibrium entropy when the thermodynamic space is broadened to include fluxes of various orders. It is thereby shown that the Pfaffian form descends from the Clausius inequality, which is regarded as equivalent to the second law of thermodynamics.

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In a recent work [1] the present author has shown, on the basis of analysis of the Clausius inequality and the Clausius notion of uncompensated heat [2], that if the Clausius uncompensated heat is taken into consideration there exists a quantity called compensation differential (differential of compensation function) whose circular integral over a cyclic process vanishes even though the process is irreversible. This compensation function becomes coincident with the Clausius entropy as the process becomes reversible. Pfaffian differential forms for this compensation function have been deduced from the balance equation for nonequilibrium entropy in Ref. [1]. It is also found that the latter is generally not in a Pfaffian form if the system is away from equilibrium and the processes are nonlinear. Since the deduction for the differential forms for the compensation function has been indirectly made through the nonequilibrium entropy, it is judged not fully satisfactory. We remove this unsatisfactory feature by presenting a balance equation for the compensation function itself and derive a Pfaffian differential form for it by assuming a form for the uncompensated heat accompanying the irreversible processes involved in the cycle. This assumption is tantamount to clarifying the meaning of uncompensated heat for the irreversible processes of interest.

Carnot's theorem [3] made it possible for Lord Kelvin [4] to discover that there exists a universal thermodynamic temperature scale independent of thermometric materials. We now know that this universal temperature scale can be made to coincide with the absolute temperature scale. On the basis of the Carnot theorem and the thermodynamic temperature scale, Clausius [2], for a cyclic process which must be interpreted as global but not local, obtained an inequality

$$-\oint dQ/T \geq 0. \tag{1}$$

Here dQ is the heat transfer counted negative if it is given up by the body as a whole to the surroundings and positive if it is taken up by the body from the surroundings. The cyclic integration is over the cycle of processes. The temperature T in (1) is the temperature of the heat reservoir which is in thermal contact with the infinitesimal Carnot cycle at a point in the cyclic process for the overall cycle. Clausius [2] introduced the notion of un-

compensated heat which balances the cyclic integral on the left-hand side of the Clausius inequality (1) and is always positive, vanishing only for reversible processes. As by Clausius, it will be denoted by N . Thus we have

$$N = -\oint dQ/T \geq 0. \tag{2}$$

The uncompensated heat N may be written in the integral form for the cyclic process

$$N = \oint dN \geq 0, \tag{3}$$

where $dN \geq 0$ for all segments of the cyclic process, or it is possible to devise a cycle such that $N \leq 0$. But this would violate the second law. Hence the inequality $dN \geq 0$. Combination of (2) and (3) yields the equation

$$\oint dQ/T + \oint dN = 0. \tag{4}$$

This integral form can be cast into the differential form [5]

$$d\Psi = dQ/T + dN, \tag{5}$$

which on integration over the cycle vanishes identically:

$$\oint d\Psi = 0. \tag{6}$$

This means that in the space of variables defining the circular integral in the aforementioned integral form, the differential $d\Psi$ is an exact differential regardless of the nature of the process involved, namely, whether the process is reversible or irreversible. The quantity Ψ is called the compensation function and $d\Psi$ the compensation differential.

If the process is reversible so that $dN = 0$ identically everywhere over the cycle of processes, then

$$\oint_{\text{rev}} dQ/T = \oint_{\text{rev}} d\Psi = 0, \tag{7}$$

where the subscript rev on the integral means that the cycle is reversible. For such cases Clausius defined the entropy S_e by the formula

$$dS_e = (dQ/T)_{\text{rev}}. \tag{8}$$

The reversible compensation function Ψ_{rev} therefore coincides with the Clausius entropy S_e :

$$S_e = \Psi_{\text{rev}} . \quad (9)$$

We should distinguish the compensation function from the nonequilibrium entropy, which we reserve for the kinetic theory entropy defined by the Boltzmann H function and the information entropy used for nonequilibrium problems, since the compensation function is different from the Boltzmann entropy [7].

If we denote the internal energy change by dE and the associated work by dW , then the first law of thermodynamics for an infinitesimal process takes the following differential form:

$$dE = dQ - dW , \quad (10)$$

where the work done by the system is taken to be positive and the work done on the system by the surroundings is taken to be negative. Since the energy must be conserved in a cyclic process, reversible or irreversible, the integral form for the first law for the cycle in question is

$$\oint dE = 0 . \quad (11)$$

Therefore, the first and second laws of thermodynamics now can be phrased as a pair of vanishing integrals (11) and (6) for E and Ψ , respectively [6]. We emphasize that Ψ is not the same as the Clausius entropy nor is it the Boltzmann entropy defined in the phase space in terms of distribution functions of particle momenta and positions as shown by kinetic theory analysis [7]. It is now necessary to clarify the nature of the compensation function and a possible form for the uncompensated heat.

The circular integral (6) may be written as an integral over period τ for the cycle

$$\oint d\Psi = \int_0^\tau dt \frac{d\Psi}{dt} = 0 . \quad (12)$$

Writing the uncompensated heat in the form $dN = (dN/dt)dt$ allows to put (5) in the differential form

$$\frac{d\Psi}{dt} = T^{-1} \frac{dQ}{dt} + \frac{dN}{dt} . \quad (13)$$

Since the time derivatives in (13) are the global rates of change, it is useful to express them in local form. To this end, we write

$$\frac{d\Psi}{dt} = \int_V d\mathbf{r} \left[\frac{\partial}{\partial t} \rho \hat{\Psi} + \nabla \cdot (\mathbf{u} \rho \hat{\Psi}) \right] , \quad (14)$$

$$T^{-1} \frac{dQ}{dt} = T^{-1} \int_B d\mathcal{B} \cdot (-1) \mathbf{Q}^c = - \int_V d\mathbf{r} \nabla \cdot (\mathbf{Q}^c / T) , \quad (15)$$

$$\frac{dN}{dt} = \int_V d\mathbf{r} \rho \hat{\Xi}_c . \quad (16)$$

Here \mathbf{u} is the fluid velocity, and it is assumed that the temperature is uniform over the surface \mathcal{B} of the volume of the infinitesimal Carnot cycle which is in contact with a local heat reservoir of temperature T . It must be noted that except for the terminal infinitesimal Carnot cycles this local heat reservoir is generally not one of the heat

reservoirs of the finite Carnot cycle which is imagined to consist of infinitesimal Carnot cycles in the derivation of inequality (1) by Clausius. Here ρ denotes the mass density, \mathbf{Q}^c is the net heat flux at the surface \mathcal{B} whose positive normal direction is outward, and $\rho \hat{\Xi}_c$ is the local rate of uncompensated heat. Equation (13) and the continuity of the processes imply the balance equation for compensation function Ψ :

$$\rho \frac{d\hat{\Psi}}{dt} = - \nabla \cdot (\mathbf{Q}^c / T) + \rho \hat{\Xi}_c . \quad (17)$$

The precise nature of \mathbf{Q}^c and $\hat{\Xi}_c$ is not known at this point in development. We would now like to clarify their meanings. The meanings of \mathbf{Q}^c and $\hat{\Xi}_c$ are bound to change as our understanding of irreversible processes evolves with time when more and more refined experiments are performed.

Before we make propositions for \mathbf{Q}^c and $\hat{\Xi}_c$, we need to define some observables and their evolution equations. Some of the evolution equations are simply the mass, momentum, and energy conservation laws expressed in local form, whereas the rest of the evolution equations are constitutive equations for various fluxes such as diffusion fluxes, heat fluxes, stresses, and other higher-order fluxes deemed necessary for description of irreversible processes of interest.

Definitions: \mathcal{E} is the energy density; $\Pi = \sum_{a=1}^r \Pi_a$ is shear stress; $\Delta = \sum_{a=1}^r \Delta_a$ is the excess normal stress, namely, the excess trace part of the stress; $\mathbf{Q} = \sum_{a=1}^r \mathbf{Q}_a$ = heat flux; and \mathbf{J}_a = mass diffusion flux of species a .

Note that if the stress (pressure) tensor is denoted by \mathbf{P} , then it may be decomposed into components as follows:

$$\mathbf{P} = \sum_{a=1}^r \mathbf{P}_a = \sum_{a=1}^r (\Pi_a + \Delta_a \delta + p_a \delta) , \quad (18)$$

where $\Pi_a = (\mathbf{P}_a + \mathbf{P}_a^t) / 2 - \frac{1}{3} \delta \text{Tr} \mathbf{P}_a$, $\Delta_a = \frac{1}{3} \text{Tr} \mathbf{P}_a - p_a$, p_a is the partial pressure of species a , and δ is the unit second-rank tensor. The fluxes including Π_a , Δ_a , \mathbf{Q}_a , and \mathbf{J}_a will be denoted collectively by $\Phi_{ka} \equiv \rho \hat{\Phi}_{ka}$ ($k \geq 1$), which are suitably ordered with regard to index k . Since their ordering is not important for our discussion here, we will not elaborate on it. There can be as many fluxes as necessary for an appropriate description of irreversible processes of interest. They are included in the set $\{\Phi_{ka} : 1 \leq a \leq r; k \geq 1\}$. Partial pressures p_a and the total pressure $p = \sum_{a=1}^r p_a$ appear as constitutive parameters in the phenomenological theory. These are local variables, and are measured by putting the infinitesimal cycle of interest in mechanical equilibrium with the local heat reservoir which is at partial pressures p_a ($1 \leq a \leq r$) and temperature T . This manner of quantifying partial pressures means that the pressure will have a distribution over the finite cycle composed of the infinitesimal cycles, for which the pressures are quantified by the means just indicated. We make the following propositions for the conservation laws and the evolution equations for fluxes.

Proposition 1. The mass, momentum, and energy conservation laws for an r -component fluid mixture have the following local forms:

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u} \quad \text{or} \quad \frac{\partial \rho}{\partial t} = -\nabla \cdot \rho \mathbf{u}, \quad (19)$$

$$\rho \frac{d}{dt} c_a = -\nabla \cdot \mathbf{J}_a, \quad (20)$$

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla \cdot \mathbf{P} + \rho \mathbf{F}, \quad (21)$$

$$\rho \frac{d\mathcal{E}}{dt} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a, \quad (22)$$

where \mathbf{F} is the external force per volume per mass at position \mathbf{r} , and \mathbf{F}_a is its species component; v is the specific volume $v = \rho^{-1}$; $c_a = \rho_a / \rho$ is the mass fraction of species a ; and $d/dt = \partial/\partial t + \mathbf{u} \cdot \nabla$, the substantial time derivative in the reference frame moving at the fluid velocity \mathbf{u} .

These local forms are easily derivable from the mass, momentum, and energy conservation laws by using the method of continuum mechanics. Coupled with these conservation laws, there are evolution equations for various fluxes including those appearing in these conservation laws, namely, \mathbf{J}_a , \mathbf{Q} , or \mathbf{Q}_a , and \mathbf{P} or \mathbf{P}_a . The forms of such evolution equations depend on the substance in hand. They are therefore constitutive equations which must be clarified on the basis of investigations of material properties. Their forms cannot be arbitrary, but are subject to thermodynamic laws. Such evolution equations for fluxes are collectively written as follows.

Proposition 2.

$$\rho \frac{d}{dt} \hat{\Phi}_{ka} = -\nabla \cdot \psi_{ka} + Z_{ka} + \Lambda_{ka} \quad (1 \leq a \leq r; k \geq 1), \quad (23)$$

where ψ_{ka} is the flux of Φ_{ka} , Z_{ka} is a collection of terms including the thermodynamic force driving the flux Φ_{ka} , and Λ_{ka} is the dissipation term responsible for energy dissipation in the system.

We have written them out as separate terms, since they have different physical interpretations and origins. Phenomenologically, these terms must be chosen so as to satisfy the second law of thermodynamics which in the present formulation is represented by the inequality for the local uncompensated heat production per unit time

$$\rho \Xi_c \geq 0. \quad (24)$$

Some examples for the kinematic term Z_{ka} and the dissipation term Λ_{ka} can be found in Ref. [1]. These quantities allow us to understand the meanings of \mathbf{Q}^c and $\hat{\Xi}_c$ appearing in the compensation function balance equation (17).

Since mass fractions c_a and fluxes $\hat{\Phi}_{ka}$ ($1 \leq a \leq r; k \geq 1$) are treated as independent thermodynamic variables together with \mathcal{E} and v , each of them must be paired with its conjugate intensive variable. We will denote them by $\hat{\mu}_a$ for c_a and by X_{ka} for $\hat{\Phi}_{ka}$. The former will turn out to be the chemical potential of species a and the latter the generalized potentials. The parameter $\hat{\mu}_a$ can in principle be quantified by setting the infinitesimal cycle of interest in material equilibrium with the local heat reservoir of composition c_a ($1 \leq a \leq r$), temperature T and partial pressures p_a . Similarly, X_{ka} can in principle be quantified by making the differences in $\hat{\Phi}_{ka}$ vanish across the bound-

aries between the infinitesimal cycle of interest and the local heat reservoir of temperature T , pressure p , and chemical potentials $\hat{\mu}_a$ ($1 \leq a \leq r$). Therefore, intensive parameters T , p , $\hat{\mu}_a$, and X_{ka} characterize the contact conditions between the infinitesimal cycle of interest and the local heat reservoir which is under control of the observer, that is, a part of the local heat reservoir may serve as the measuring instruments for temperature, pressure, chemical potentials, and generalized potentials. These parameters are therefore contact quantities. We make the following proposition for \mathbf{Q}^c and $\hat{\Xi}_c$.

Proposition 3. There is a set of intensive parameters X_{ka} and $\hat{\mu}_a$ conjugate to fluxes $\hat{\Phi}_{ka}$ and mass fractions c_a , respectively, such that the compensated heat flux \mathbf{J}_c and the uncompensated heat production $\rho \hat{\Xi}_c$ are given by

$$\begin{aligned} \mathbf{J}_c &= \mathbf{Q}^c / T \equiv \sum_{a=1}^r \mathbf{Q}_a^c / T \\ &= \sum_{a=1}^r T^{-1} \left[\mathbf{Q}_a - \hat{\mu}_a \mathbf{J}_a + \sum_{k \geq 1} X_{ka} \psi_{ka} \right], \end{aligned} \quad (25)$$

$$\begin{aligned} \Xi_c &= \rho \hat{\Xi}_c \equiv -T^{-1} \sum_{a=1}^r \left[(\mathbf{P}_a - p_a \delta) : \nabla \mathbf{u} + \mathbf{Q}_a^c \cdot \nabla \ln T \right. \\ &\quad \left. + \mathbf{J}_a \cdot (\nabla \hat{\mu}_a - \mathbf{F}_a) \right. \\ &\quad \left. - \sum_{k \geq 1} \psi_{ka} \cdot \nabla X_{ka} \right] \\ &\quad + T^{-1} \sum_{a=1}^r \sum_{k \geq 1} X_{ka} (Z_{ka} + \Lambda_{ka}) \geq 0. \end{aligned} \quad (26)$$

Since Ξ_c must be positive semidefinite by the requirement of the positive uncompensated heat production—the second law of thermodynamics, inequality (24) for Ξ_c dictates the acceptable forms for the kinematic Z_{ka} and the dissipation terms Λ_{ka} of the evolution equations for fluxes, and hence for the evolution equations for the fluxes. The proposition for the compensated heat flux \mathbf{J}_c defines the meaning of \mathbf{Q}^c , whereas the proposition for uncompensated heat production Ξ_c defines what we mean by the uncompensated heat originally introduced by Clausius but left unelucidated.

The compensation function balance equation now can be expressed in a Pfaffian form in space $\mathcal{G} \equiv (\mathcal{E}, v, c_a, \hat{\Phi}_{ka}; 1 \leq a \leq r; k \geq 1)$. It can be done quite easily by eliminating the compensated heat flux and the uncompensated heat production by using the balance and evolution equations (19)–(23). After some straightforward algebraic steps, from (17), (25), and (26) we obtain the differential form

$$\begin{aligned} d_t \hat{\Psi} &= T^{-1} \left[d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a \right. \\ &\quad \left. + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d_t \hat{\Phi}_{ka} \right], \end{aligned} \quad (27)$$

where $d_t = d/dt$ and $p = \sum_{a=1}^r p_a$. This is the Pfaffian form for the compensation function consistent with the form of uncompensated heat proposed; it is the main aim of this work to give the thermodynamic basis to this

differential form, which has not been adequately done until now. This differential form has the following property:

$$\int_0^\tau dt \rho \frac{d\hat{\Psi}}{dt} = \oint \rho d\hat{\Psi} = 0, \quad (28)$$

which can be deduced, on account of continuity, from (11), since

$$\begin{aligned} \int_0^\tau dt \frac{d\Psi}{dt} &= \int_0^\tau dt \int_V d\mathbf{r} \left[\frac{\partial}{\partial t} \rho \hat{\Psi} + \nabla \cdot \mathbf{u} \rho \hat{\Psi} \right] \\ &= \int_V d\mathbf{r} \int_0^\tau dt \rho \frac{d\hat{\Psi}}{dt} = 0. \end{aligned} \quad (29)$$

The vanishing circular integral implies that the differential form $d_t \hat{\Psi}$ in (27) is exact in space \mathfrak{G} , and thus $\hat{\Psi}$ is a state function in \mathfrak{G} . This state function is determined as an integral of the Pfaffian form (27) once the constitutive relations for T^{-1} , p , $\hat{\mu}_a$, and X_{ka} are given in space \mathfrak{G} . As X_{ka} vanishes for all k and a , $d_t \hat{\Psi} \rightarrow d_t \hat{\Psi}_{\text{rev}} = d_t S_e$, where S_e is the equilibrium (Clausius) entropy, and we recover the equilibrium thermodynamic relation. However, at nonequilibrium or for irreversible processes $\hat{\Psi} \neq S_e$. In fact, the local equilibrium assumption for $d_t S_e$ is recovered if it is assumed that $d_t \hat{\Phi}_{ka} = 0$ for all k and a . If it is further assumed that there are only the usual 13 moments ($2+11r$ moments for an r -component mixture); Z_{ka} consists of only the thermodynamic force term for Φ_{ka} ; X_{ka} , and Λ_{ka} are linearly proportional to $\hat{\Phi}_{ka}$ (see Ref. [1] for the proportionality coefficients), then the mathematical structure of linear irreversible thermodynamics is recovered from the

present theory. Therefore, the theory of linear irreversible thermodynamics is contained in the present theory. Kinetic theory analysis [7] of the Boltzmann statistical entropy shows that it is different from the compensation function and does not have the Pfaffian differential form in \mathfrak{G} like (27) for $\hat{\Psi}$.

In conclusion, we have shown how the Pfaffian form (27) for the compensation function arises in a way consistent with the second law of thermodynamics, and also how to set the evolution equations for fluxes under the umbrella of the second law of thermodynamics in the sense that Z_{ka} and Λ_{ka} must be such that Ξ_c is positive semidefinite and at the same time the evolution equations for fluxes are consistent with the Pfaffian form for the compensation function (27). The key to this result is proposition 3 for \mathbf{Q}^c and Ξ_c . It must be noted that in this phenomenological approach the parameters T , p , $\hat{\mu}_a$, and X_{ka} are constitutive parameters which must be postulated on phenomenological grounds. In this connection, note that T^{-1} is usually replaced by the caloric equation of state. If the compensation function $\hat{\Psi}$ is interpreted as coincident with the nonequilibrium entropy in extended irreversible thermodynamics (EIT) [8,9], then propositions 1–3 presented provide the thermodynamic foundations for the extended Gibbs relation for the nonequilibrium entropy in EIT in a rather general context.

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$-d\Psi \Rightarrow d\Psi$. This change in sign does not alter the essential nature of the compensation function.

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